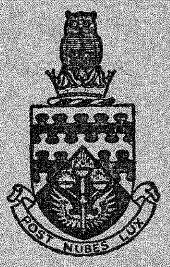

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AN EXAMINATION OF THE METHODS OF MIXING PEROXIDES INTO POLYTHENE TO FORM POLYMER NETWORKS

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SUMMARY

In the production of peroxide cross-linked polyethylenes it is customary to introduce the organic peroxide by the hot milling process. Inevitably some peroxide is lost by volatilization and the process is, therefore, difficult to standardize.

In this paper, the efficiencies of the processes in which the peroxide is introduced by wet and dry powder mixing are compared with the efficiency of the normal method of mill mixing. It is shown that in both the wet and dry processes the loss of peroxide is avoided, but that the dry mixed material shows inhomogeneities in the cross-linked state.

Contents

1. Introduction

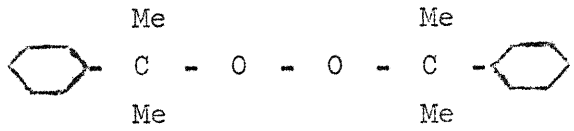
In recent years it has been found possible to cross-link ethylene polymers by the production of free radicals within the bulk polymer. This can be done either by the incorporation of a free radical-liberating substance (e.g. certain organic peroxides[2,3,4,5,6]), followed by the application of heat, or by the use of high energy radiation[1]. The polymer subjected to such treatment exhibits properties not found in a normal thermoplastic polythene. Its solubility is substantially reduced and it shows rubber-like behaviour at temperatures above its melting point. The extent to which these properties occur is dependent upon the degree of cross-linking. In the case of peroxide cross-linked systems, the number of cross-links present for any given amount of peroxide depends markedly on the efficiency of incorporating and mixing the peroxide into the polymer.

This Note reports the results of an investigation into the efficiency of three mixing methods, namely, dry mixing, slurry mixing, and milling. Two independent methods of assessing the extent of network formation were employed, namely, the determination of sol/gel fractions by extraction in xylene at 137°C, and that of elastic modulus by simple load/extension measurements at 137°C. The latter method yields quantitative data on the actual extent of network formation, whilst the former method, in the absence of a detailed knowledge of the molecular weight distribution in the non-cross-linked material, yields only semi-quantitative data on the extent of cross-linking.

2. Materials

(i) Di-cumyl peroxide

The peroxide chosen was Bis ($\alpha\alpha$-dimethylbenzyl) peroxide, or D.C.P.



D.C.P. is a white crystalline solid, melting at 39°C. The technical product used in this investigation was supplied by The Hercules Powder Co. Ltd., as 'Perkadox S.B.' and contains 5 to 10% impurities, probably comprising cumyl hydroperoxide, cumyl alcohol, and acetophenone. This peroxide, amongst others, decomposes at elevated temperatures into free radicals[9] which react with the polythene chains to form polymer radicals; the radicals then terminate, it is believed, by forming cross-links between polymer chains, by chain scission, or by disproportionation into double bonds.

This particular peroxide was selected as it is among the best of the organic peroxides with respect to cross-linking effectiveness[2,6],

safety of handling, and availability. Its low melting point is convenient in ensuring that the solid melts on hot mill rolls and easily disperses into the molten polythene.

To give visual aid to the mixing processes, the D.C.P. was firstly treated in the following manner. It was gently melted at 45 - 50°C and a red rubber-pigment (1%) was dispersed into the melt which was then cooled and recrystallized. The crystals were then carefully ground to give a fine red powder.

(ii) Polythene

The polythene used was a high density variety, 'Hostalen G.W. (Natural)', which was powdered, to facilitate compounding, by Telcon Plastics Ltd.

3. Experimental procedure

Mixing methods

(i) Dry blending

Given amounts of the red peroxide powder were manually stirred into the polythene powder. The mix was considered good when it had achieved a visually homogeneous pink colouration.

(ii) Slurry mixing

Given amounts of the peroxide were dissolved in acetone and poured into a Dresdel bottle charged with polythene powder. Sufficient acetone was used to form a slurry with the polythene and the whole mix was vigorously agitated to give homogeneous colouration. The acetone was then removed by passing air through the slurry until a dry powder was obtained.

(iii) Milling

Milling was carried out on a 6" × 12" rubber mill running with a surface temperature of 130 - 135°C. A hide of known weight was formed from the polythene powder and given amounts of peroxide were added to it. The mix was considered good when homogeneous pink colouration was achieved; this was obtained in less than 5 minutes from the time of the addition of the peroxide.

Curing

In all cases the compounds were placed in a mould whose temperature was 160°C and pressed into flat sheets less than 2 m.m. thick. Preliminary experiments showed that 15 minutes at this temperature was a suitable cure time and this was adhered to throughout. On completion of cure the mould

was cooled under pressure and the sheet then removed.

4. Measurement of the extent of network formation

(i) Sol/Gel contents

Polythene is normally fully soluble in xylene at elevated temperatures but as cross-linking develops so the polymer becomes more and more insoluble. This property was used as one method of checking the amount of network formation.

Extraction

A normal Soxhlet extractor was used with xylene (BP. 137°C). Experiments using irradiated polythene of known dosage showed that constant gel fractions were achieved after 16 hours extraction. This agrees approximately with results obtained by Baskett[7]. Experiments on irradiated polythene showed that there was no significant difference in results of extractions carried out in nitrogen rather than air (See figure 1).

As a result of these preliminary tests, a standard extraction of 16 hours in air was used throughout. The extractions were carried out on small discs ($< \frac{1}{2}''$ diameter) punched from the moulded sheet. Each disc was weighed ($\sim$ 0.0600 gms) before being placed in individual gauze buckets inside the Soxhlet. Twelve discs were used in each extraction.

Removal of solvent after extraction

To obtain an accurate weight loss for each disc, it was necessary to ensure that no solvent remained before re-weighing. Test showed that constant dry weights were achieved after six hours vacuum drying at 70 - 80°C, and this became standard procedure. On completion of extraction and drying, the discs were removed from their buckets and re-weighed.

The ratio $W2/W1$ is the gel fraction, where W1 is the dry weight before extraction and W2 is the dry weight after extraction. $1 - \frac{W2}{W1}$ is the sol fraction.

(ii) Elastic modulus

Polythene normally becomes liquid-like above its melting point (105 - 115°C) but as cross-linking occurs and increases, so the polymer exhibits rubber-like elasticity and the modulus can be related to degree of cross-linking.

Treloar[8] quotes the approximate relation, based on the kinetic theory of rubber-like elasticity, as follows:-

$$\frac{L}{Ao} = \frac{\rho RT}{M_c}\left(\lambda - \frac{1}{\lambda^2}\right)$$

where L = load

Ao = original cross-sectional area

ρ = density

R = gas constant

T = absolute temperature

M_c = degree of cross-linking

λ = linear extension ratio

This relation is the simplest form predicted by the kinetic theory and has to be modified to give more complex forms, which take into account the initial molecular weight of the non-cross-linked material and other factors. In this investigation, however, the need is for comparative rather than absolute assessment of network formation and the simplest relation is therefore used.

The apparatus used is shown diagrammatically in figure 2. It consisted of a Liebig condenser adapted to form a heated jacket around the test piece. The jacket was heated by means of xylene vapour passed around the outside of the inner tube whilst a slow stream of nitrogen was passed through the inner tube to ensure that the test piece did not oxidize. The temperature inside the tube was 137°C, ±1°C.

Dumbells were cut from the moulded sheets and hung in the inner tube. Weights were hung on these dumbells and extensions between two bench marks were measured by means of a cathetometer.

5. Results and discussion

The results are shown in Table 1, and graphically in Figures 3 and 4. Figure 3 shows the plot of sol fraction against parts per hundred of DCP for each of the mixing methods, and although sol fraction has not been correlated numerically to degree of cross-linking, the families of curves are similar and place the mixing methods in the same order of efficiency as the plot of M_c (from load/ext. experiments), against parts per hundred DCP shown in Figure 4.

Milling a given amount of peroxide into polythene gives less network polymer than the other two methods investigated, but this is almost certainly due to a loss of part of the peroxide by volatilization whilst on the mill, rather than to inefficient mixing.

The amount of network polymer obtained by the other two methods is almost identical but it was noted that at the lower concentrations of DCP the dry hand mixed materials were less homogeneous than both the

slurry and mill mixed materials. This was particularly noticeable when carrying out load/extension measurements, where at the heavier loadings the parallel section of the dumbell test piece became quite inhomogeneous for dry hand mixed materials but not for the slurry or mill mixed materials.

6. Conclusions

It is shown that of the three methods investigated the slurry mixing achieves a higher degree of network formation than milling, without suffering from the lack of homogeneity that dry hand mixing exhibits. Slurry mixing, however, requires the original polythene to be in powdered form whereas milling does not. Commercially the cost of powdering would be greater than the addition of extra peroxide to compensate for volatization on the mill. For laboratory preparation of samples it does seem that slurry mixing may have real advantages over the other methods investigated.

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Table 1

Results

p.p.h. DCP	Mixing method	Sol fraction (Average of 6 results)	M_c by modulus (Average of 2 results)
2	Dry	0.372	16,700
$2\frac{1}{2}$	Dry	0.149	8,200
3	Dry	0.111	3,650
$4\frac{1}{2}$	Dry	0.062	3,900
6	Dry	0.056	2,800
2	Slurry	0.388	17,400
$2\frac{1}{2}$	Slurry	0.158	10,800
3	Slurry	0.119	6,750
$4\frac{1}{2}$	Slurry	0.069	3,960
6	Slurry	0.058	2,740
2	Milled	0.529	20,300
$2\frac{1}{2}$	Milled	0.273	12,800
3	Milled	0.178	8,600
$4\frac{1}{2}$	Milled	0.089	5,670
6	Milled	0.060	4,040

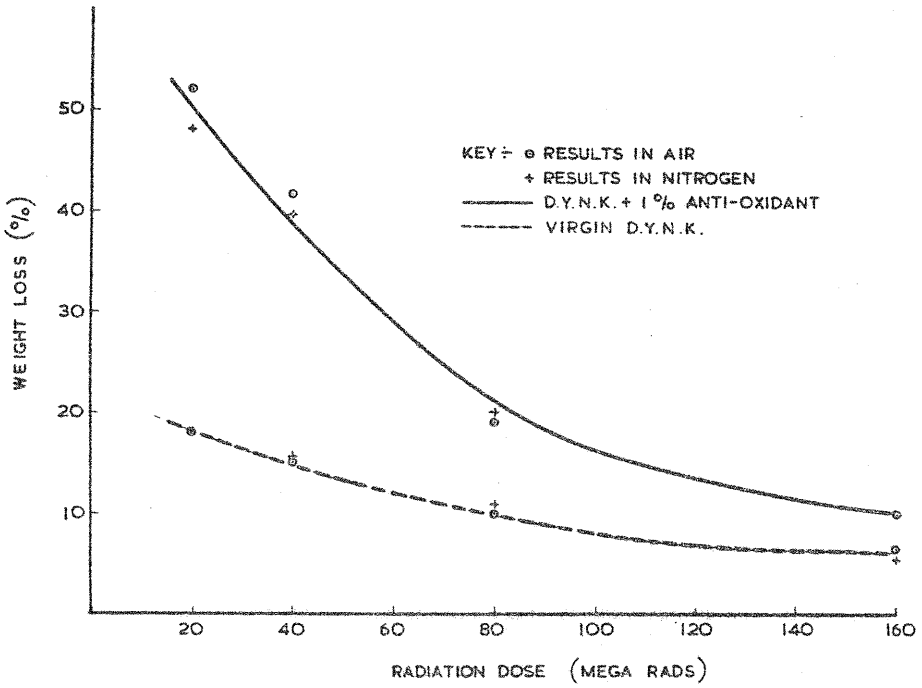

Figure 1 EXTRACTION OF IRRADIATED POLYTHENES IN XYLENE USING ATMOSPHERES OF AIR AND NITROGEN

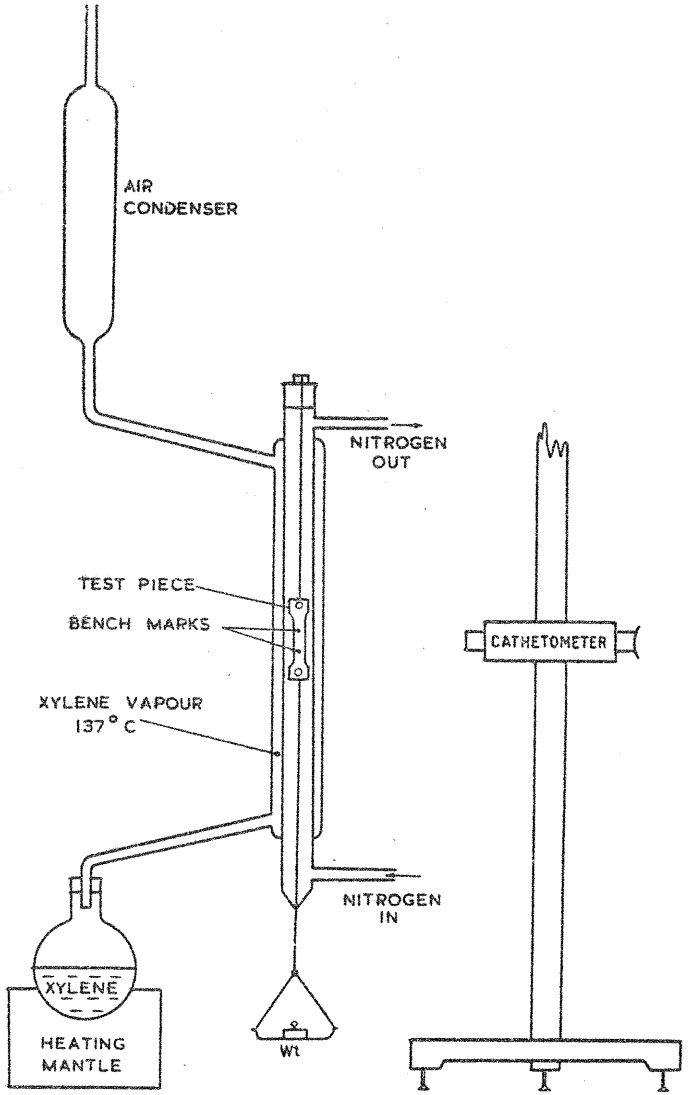

Figure 2 APPARATUS USED IN THE MEASUREMENT OF THE ELASTIC MODULUS OF CROSS-LINKED POLYTHENE

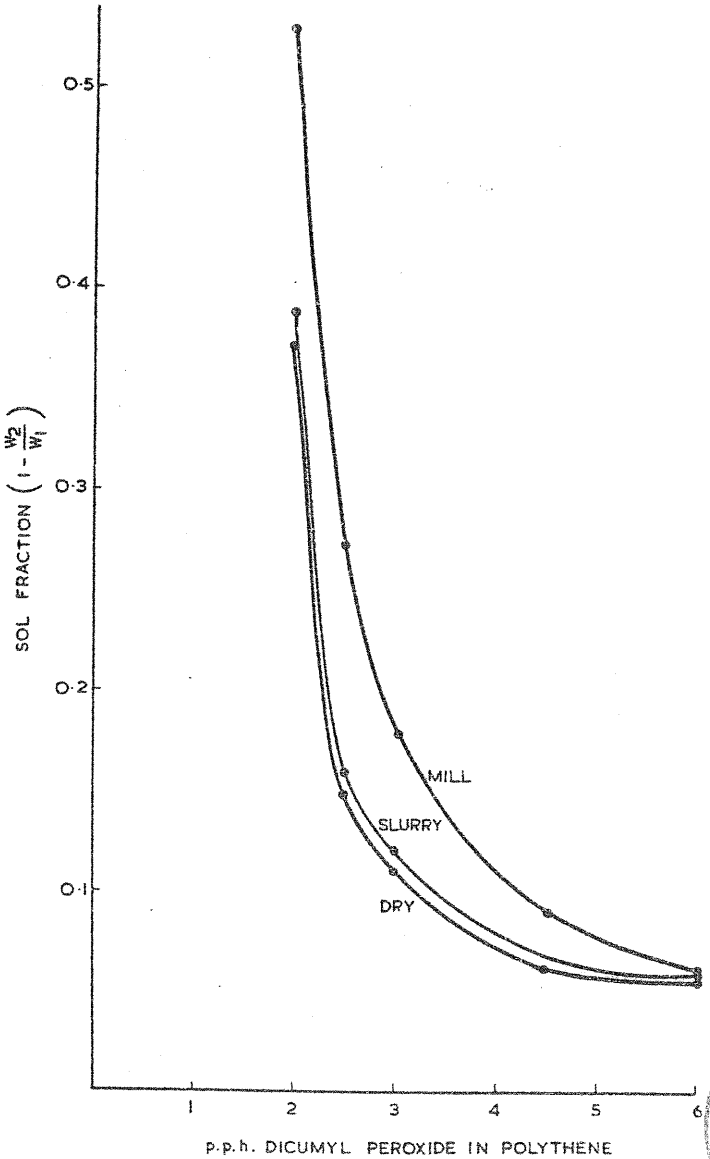

Figure 3 COMPARISON OF MIXING METHODS USING THE PLOT OF SOL FRACTION AGAINST p.p.h. DICUMYL PEROXIDE

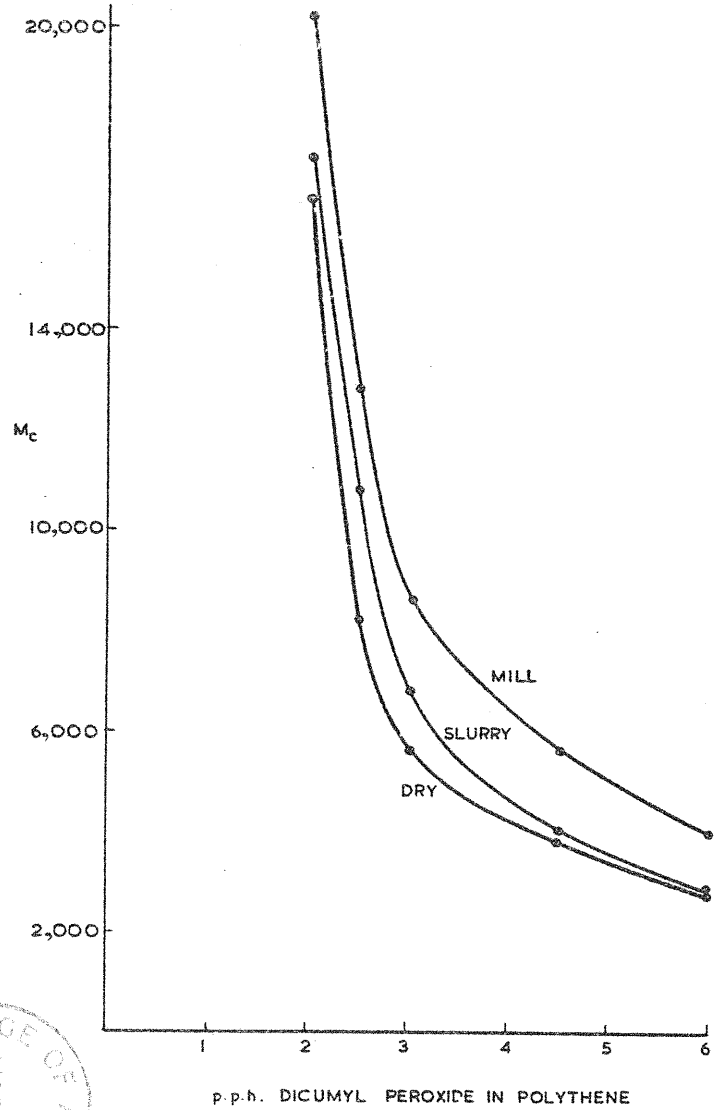

Figure 4. COMPARISON OF MIXING METHODS USING THE PLOT OF M_c AGAINST p.p.h. DICUMYL PEROXIDE